APPLICATIONS OF SOLID STATE CHEMISTRY TO MINERALS AND MINERAL PROCESSING

By

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Summary of published research, 1968-2001

Throughout his career, a consistent aim of the candidate's research has been to apply the methods of solid state chemistry to solve metallurgical and mineral processing problems, while maintaining and developing his disciplinary skills and techniques. The work has thus involved parallel inputs to fundamental research and to applied research for mining and manufacturing companies.

The candidate's scientific specialisation is in crystallography and phase equilibria. In crystallography he has worked on the determination of the structures of complex minerals and synthetic materials and the elucidation of structural principles relating different structure types. The structures are often complicated by problems such as microdomain formation, pseudosymmetry, metamictisation and diffuse diffraction effects due to short range order and the candidate has developed expertise in solving and refining such structures, where conventional methods cannot be applied. In phase equilibria studies he has specialised in the determination of high temperature solid/gas phase relations in systems involving elements in different oxidation states. He has developed appropriate experimental procedures involving controlled gaseous atmospheres and microbalance techniques and has applied these techniques to reactions of industrial importance.

The attached list of publications reflects the candidate's specialised expertise in the fields of crystallography and phase equilibria. The publications can be grouped into three main categories:
1. Postgraduate and postdoctoral research (and ongoing collaboration).
2. Structure systematics in mineral and synthetic systems.
3. Fundamental support for mineral processing projects.

In the first category is included PhD studies at the University of Tasmania on structures, magnetic and spectroscopic properties of halide complexes (papers 1-5, 9), postdoctoral studies on chalcogenides (papers 6-8, 12, 20, 21, 23) and ongoing collaborative studies with Uni. of Tasmania postgraduate students (papers 59, 64, 67, 75, 76, 80, 81, 91).

A major aspect of the work on halides involved the interpretation of magnetic and spectroscopic properties of binuclear halide complexes of molybdenum, $A_3Mo_2X_9$, X=Cl, Br, I in terms of modifications to the geometry of the $Mo_2X_9^{3-}$ complex anion due to change of size of the monovalent A cation (e.g. K, NH_4, Rb, Cs, Me_4N, Me_3NH, Me_2NH_2, $MeNH_3$, $EtNH_3$). At the time of the candidate's PhD studies, there was only limited structure information available on these compounds, partly due to the difficulty of obtaining single crystals for structure refinements. More recently, he has applied Rietveld analyses to X-ray diffraction data from powder samples to obtain accurate structure information on many compounds in the series. This has enabled different models for magnetic interactions to be critically evaluated against the measured magneto-structural properties, leading to a detailed understanding of the role of metal-metal bonding in controlling the properties of these systems (papers 75, 80).

The candidate's postdoctoral studies on chalcogenides have focused on the phase equilibria and structure-property relationships in the Ba-Fe-S system. Particularly

noteworthy was his elucidation of the structural principles governing the structures of ordered superstructures in the composition range $Ba_{1+x}Fe_2S_4$, $0.06<x<0.14$ (papers 20, 21). The homologous series of structures, $Ba_pFe_{2q}S_{4q}$, p, q integers, that span this composition range, represented one of the first published examples of 'vernier structures'.

The second category of publications includes structure determinations and crystal chemistry studies carried at at CSIRO and at the CNRS laboratoire de Crystallographie at Grenoble. A major theme has been the elucidation of structure systematics and crystal chemistry in minerals, particularly from Australian localities. The emphasis on titanate minerals links to the candidate's applied research involvement in titania mineral processing. His work on the extended family of minerals related to crichtonite (papers 25, 27, 31, 32, 35, 36, 53, 56, 96, 104) has provided an understanding of the structure-composition relations in this family of complex minerals (e.g. formula of mathiasite is $(K_{0.62}Na_{0.14}Ba_{0.14}Sr_{0.10})(Ti_{12.90}Cr_{3.10}Mg_{1.53}Fe_{2.15}Zr_{0.67}Ca_{0.29}(V,Nb,A1)_{0.36})O_{38}$).

An important outcome of the fundamental study on these minerals was the identification by the candidate of a crichtonite-related compound as an impurity phase in a new process for ilmenite upgrading currently that was commercialised in Australia in 1996. The impurity phase was adversely affecting the product quality and jeopardising the success of the project. From his detailed knowledge of the minerals, the candidate was able to define its stability field and to propose process modifications to avoid its formation, thus contributing to the successful development of a process worth tens of millions of dollars per year (ilmenite upgrading with removal of radionuclides).

Structure characterisations were undertaken on a number of titania-containing minerals associated with gold mineralisation at Kalgoorlie (papers 38, 47, 55, 61) and Hemlo, Canada (papers 68, 79 90) and alluvial diamonds at Argyle (paper 74). Collaboration with Professor S. Haggerty at the Uni. of Massachusetts led to the structural characterisation of titanate minerals of significant geological importance in relation to metasomatic mineral complexing in the upper mantle (papers 66, 70, 79). An important contribution to lunar mineralogy was made by characterising tranquillityite, the only new mineral to be discovered in lunar rocks. The candidate recognised that the mineral had undergone metamictisation due to radiation damage from contained uranium, and he restored the structure by controlled heating in sealed tubes prior to X-ray analysis (paper 29). A feature of these mineral studies is that they allowed a number of new species to be characterised for submission to the International Mineral Commission. The candidate made major contributions to proposals for the naming of the new minerals loveringite, tomichite, tivanite, lucasite, hawthorneite, hemloite and haggertyite (papers 37, 38, 47, 74, 78, 79, 105), as well as the revalidation of pseudorutile (paper 94).

Studies at CNRS, Grenoble focused on the structures of materials such as perovskites and ferrites with potentially expoitable physical properties (papers 45, 46, 49, 51, 57, 85, 114, 118). A detailed knowledge of the atomic arrangements in these materials was essential to interpret their properties and predict device applications. The structures of a number of the phases studied were complicated by short range order and microdomain formation and the candidate had to develop specialised analytical procedures for extracting detailed structure information from the diffraction data.

The candidate's experience in solving complex structures led to an invitation by Dr. T. Willis at AERE, Harwell, to solve the structure of uranium oxide, U_4O_9, used in fuel rods for nuclear reactors. The huge structure, containing over 800 atoms in the basic structure motif, had resisted numerous attempts at solution over more than 20 years. The structure was solved using single crystal neutron diffraction data provided by Willis (papers 60, 65). Another example of an invitation to work on difficult-to-solve structures was from the University of Melbourne Physics Dept., to work on new cesium titanate phases, important as potential host matrices for disposal of radioactive waste elements. The phases had resisted attempts to characterise them using electron diffracion/microscopy. The candidate determined the structures of three new phases using a combination of powder and single-crystal X-ray and neutron diffraction data, and established the short-range ordering of the cesium atoms (papers 58, 69, 71, 84).

The third category of publications concerns fundamental studies using crystallography, phase equilibria and electron microscopy/microprobe techniques to directly support applied research on titania mineral processing and other processes. Of prime importance in this work were the high temperature phase equilibria and X-ray diffraction studies relevant to ilmenite upgrading. In addition to phase studies on the Fe-Ti-O system under reducing conditions relevant to plant operation (papers 13, 16-19, 43) the effects of Mn, Mg and V impurities on phase equilibria were studied (papers 26, 30, 93) as well as phase modifications resulting from addition of sulphur during reduction (papers 40, 41, 42). The results of these phase studies have been used extensively by companies operating ilmenite upgrading plants in Western Australia. A second aspect of the support research for ilmenite upgrading has been structural studies on titanate phases that form during high temperature processing. This has involved detailed structure characterisations of complex intergrowth and rutile-related superstructure compounds (papers 10, 11, 15, 24, 28, 33, 34, 39, 43, 98, 103) as well as studies on pseudobrookite-related phases formed during reduction (papers 14, 93) and oxidation (papers 106, 112).

In addition to basic research supporting high temperature commercial processing of titania minerals, the candidate has carried out fundamental studies supporting hydrometallurgical processing (papers 77, 88, 95) and natural weathering (papers 22, 47, 52, 54, 62, 94, 111, 116) of titania minerals. His structural characterisation of the highly disordered mineral pseudorutile, and his proposed two-stage model for ilmenite alteration, involving the formation of pseudorutile as an internediate alteration phase, is widely accepted and referred to in the literature. His publication list also includes some review articles describing the application of X-ray diffraction to mineral processing problems, and the processing and uses of titania-bearing minerals and other minerals in heavy mineral sands deposits (papers 87, 89, 92).

Statement of the candidate's contributions

Most of the papers given in the list of publications have one or more co-authors. However in the majority of publications (100 out of 118) I wrote the paper and carried out the major part of the work reported. In the case of the other publications, I either supervised the students involved or collaborated with colleagues and provided both experimental input and written contributions. Papers written by students that I co-supervised are #67, 76, 84 and 110 in the publication list. Papers written primarily by colleagues are #23, 34, 39, 41, 42, 60, 61, 66, 72, 78, 80, 94, 97, 100.

Signed 

Ian E. Grey

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Since joining CSIRO I have had the pleasure of maintaining an active collaboration with Peter by working with a number of his later students. I have particularly appreciated an ongoing close association with Rob Stranger, one of Peter's PhD students now working at the ANU Department of Chemistry.

While still at the University of Tasmania, David Wadsley at CSIRO's Division of Mineral Chemistry provided support and encouragement and organised for me to spend a Post Doc at the University of Texas, where I benefited greatly from working with Hugo Steinfink. On joining CSIRO in 1970 I worked under Alan Reid who stimulated my interest in applying solid state chemistry techniques to mineral processing problems. I greatly appreciated his help and benefited from his enthusiastic approach to research.

Jean Claude Joubert, Massimo Marezio and Catherine Bougerol have been very supportive of my research conducted at the CNRS Laboratoire de Cristallographie, Grenoble. I have enjoyed close research collaboration with them and other scientists during a number of visits to Grenoble. I also appreciate greatly the close working relations I have had with a number of research colleagues, including Robert Roth, Les Bursill, Lachlan Cranswick, Ian Madsen, Christina Li, Gus Mumme, John Watts, Steve Haggerty, Bryan Gatehouse, Bernard Hoskins and Ernie Nickel.

I.E. Grey Publications and Patents

1. Refereed Publications

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2. Patents

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